Selenium Concentrations in Alfalfa From Several Sources Applied to a Low Selenium, Alkaline Soil[1]

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ABSTRACT

Two laboratory-prepared ferric hydroxy bi-selenites and $CuSeO_3$ applied to Portneuf silt loam in the field provided slowly available Se to alfalfa, resulting in Se concentration adequate but nontoxic for livestock. These materials have potential as Se fertilizers at low application rates. The ferric hydroxy bi-selenites offer little or no advantage over $CuSeO_3$. Se from $BaSeO_4$ alone, $BaSeO_4$—$BaSO_4$ mixtures, and $CuSeO_4$ was absorbed by alfalfa in concentrations toxic to livestock. A small fraction of applied elemental Se was available immediately after application, providing adequate Se to alfalfa for livestock. The remaining elemental Se was rather inert, and supplies only slightly more Se to alfalfa than did the untreated soil the year following application.

Additional Key Words for Indexing: white muscle disease, ferric hydroxy bi-selenites, copper selenite, selenites, copper selenate, selenates.

THE DISCOVERY that Se is required for normal animal nutrition stimulated considerable related research. General and detailed maps of the Se content of forage and hay crops grown in the USA have been published (4, 12) as well as maps relating the occurrence of white muscle disease (WMD), a Se-responsive myopathy (14), to areas known to produce low Se forage (12, 15). The minimal Se concentration required in the animal diet ranges between 0.03 and 0.10 ppm depending upon the vitamin E level in the diet and other factors (1). Many consider 0.10 ppm Se as a safe minimum. Se concentrations above 3 to 4 ppm are toxic (17), and small applications of Se

have repeatedly produced plant concentrations of Se toxic to livestock (3, 8, 9, 12, 15). Where total Se concentrations in the soil in the Central United States range from 2 to 13 ppm, Se toxicity problems have occurred repeatedly (13).

Current regulations do not permit the direct addition of Se to animal feeds. Stockmen frequently use Se injections to prevent WMD in lambs and calves. Se compounds as soil additives can be used to provide plants with protective but nontoxic Se concentrations. The application of Na_2SeO_3 to acid and neutral soils has successfully prevented WMD in animals consuming the forage produced. However, application rates must be carefully controlled to avoid plant concentrations toxic to livestock (3, 7). Se treatment of alkaline soils may be especially difficult, because Se compounds may oxidize to form soluble selenates in an alkaline environment (6, 12). Se concentrations toxic to animals were found in 20 plant species grown in the greenhouse on alkaline soils receiving 5 to 20 ppm Se as Na_2SeO_3, Na_2SeO_4 or organic Se in the form of ground plant material (9). Alfalfa (*Medicago sativa* L.) grown in the greenhouse absorbed Se in concentrations toxic to livestock from four of seven soils treated with Se at a 2.5-ppm rate as selenized concentrated superphosphate (6). Se concentrations toxic to animals were found in alfalfa grown in the greenhouse on Madras sandy loam soil, an acid soil, when Na_2SeO_3 treatment rates exceeded 1.0 ppm Se. Alfalfa grown in the field on the same soil treated with 1.12 kg Se/ha contained up to 2.7 ppm Se (3), a concentration range safe for livestock. Topdressing with about 0.07 kg Se/ha as Na_2SeO_3 or Na_2SeO_4 on New Zealand pasture resulted in Se concentrations toxic to livestock for periods of more than a year after application (8). In this case plant crowns apparently absorbed Se, and uptake was greater than if the Se had been applied only to the soil.

The uptake of Se from soils appears to be dependent

upon the pH of the soil. Thus, there is a need for evaluating Se compounds as soil additives to provide slow and long lasting Se availability to plants grown on alkaline soils. This paper reports results of a field study conducted to evaluate the Se availability to alfalfa (*Medicago sativa* L. 'Ranger') as influenced by the application of commercially available and laboratory prepared (ferric hydroxy bi-selenites) Se compounds to an alkaline Portneuf silt loam. Several types of additives containing Se compounds were included as suggested in the literature. $BaSO_4$ was added with Se compounds as suggested by an observation that (i) $CaSO_4$ or $BaCl_2$ applications to an alkaline soil greatly reduced Se uptake (16), and (ii) by evidence that S and Se compounds compete in plant uptake and assimilation (10, 11).

MATERIALS AND METHODS

Forty-eight field plots each 2 by 5 m were established in a 1-year old stand of alfalfa growing on an alkaline Portneuf silt loam near Kimberly, Idaho. Three replications of 16 treatments were arranged in a randomized block design. The Se-containing materials were applied July 6, 1966 after the first alfalfa cutting had been removed from the field. All materials were applied using a hand-pulled shank with a tube down the rear of the shank through which the constantly agitated aqueous suspensions of the materials were dispensed. Placement was approximately 12 cm below the soil surface in bands approximately 15 cm apart.

The commercially available materials used and the application rates are shown in Table 1. The S/Se ratio was varied to determine the effect of S on Se uptake. In addition to the listed materials, two laboratory-prepared ferric hydroxy bi-selenites were applied. These materials were prepared to be similar to slightly soluble ferric hydroxy bi-selenites thought to be present in many acid soils (7).

One of these materials was prepared by adding NH_4OH to a solution of $FeCl_3$ until excess $(OH)^-$ was present. H_2SeO_3 was then added until a slight excess was present, as detected by the drop in pH. The precipitate was allowed to age for 48 hours. It was then separated by centrifuging and washing three times with water at an approximate water:solid ratio of 25:1. It was then dried and ground to a coarse powder. This material contained 30% Se with a Fe:Se molar ratio of 1:1, and will be referred to as $(Fe)_x(OH)_y(HSeO_3)_z$. It was applied at 4 kg material/ha, equivalent to 1.2 kg Se/ha.

The second ferric hydroxy bi-selenite was prepared by adding an excess of H_2SeO_3 to a $FeCl_3$ solution and then adding NH_4OH until excess $(OH)^-$ was present. The material was then handled as described above. The resulting compound was 54% Se with a Fe:Se molar ratio of 1:2.75, and will be referred to as $(Fe)_a(OH)_b(HSeO_3)_c$. It was applied at 4 kg material/ha, equivalent to 1.62 kg Se/ha.

The Portneuf silt loam used in this study is alkaline with a pH of 7.8 and a cation exchange capacity of 24 meq/100 g in the surface 15 cm. Below 15 cm, free $CaCO_3$ is present and the pH is 8.2. The $CaCO_3$ equivalent ranges from 17 to 25% below 25 cm. The surface layer particle size distribution is 25, 54 and 21% sand, silt, and clay, respectively.

Table 1—Commercially available Se containing materials applied to alkaline Portneuf silt loam

| Carrier | S/Se | Se applied, kg/ha | | | |
		0.5	0.1	2.0	4.0
BaSeO$_4$		x	x	x	x
BaSeO$_4$ and BaSO$_4$	1	x	x	x	
BaSeO$_4$ and BaSO$_4$	10	x	x	x	
CuSeO$_4$				x	
CuSeO$_4$			x		
Element Se				x	x

Alfalfa samples were collected just before harvest during the 1966 and 1967 seasons. Samples were composed of the upper 30 cm of growth from 10 or more plants for each plot. In 1966 the second and third cuttings were sampled July 21 and September 14, respectively. The respective sampling dates in 1967 were June 21, August 8, and September 28 for the first, second and third cuttings. Samples from each plot were dried at 50C, ground to pass a 1-mm sieve, and analyzed for Se content by a fluorometric method (2).

RESULTS AND DISCUSSION

Alfalfa readily absorbed Se from $BaSeO_4$ applied to Portneuf silt loam. Se concentrations toxic to livestock were found in samples from all application rates in at least one of the five cuttings harvested over two seasons (Table 2). Evidently Se from $BaSeO_4$ on alkaline soil is as available for plant absorption as it is from Na_2SeO_4 applied to acid and alkaline soils (8, 9). Thus, use of $BaSeO_4$ would require the same precautions necessary when using soluble selenates to avoid plant concentrations of Se toxic to livestock.

Applying $BaSO_4$ with $BaSeO_4$ at a S/Se ratio of 1 had no effect on the Se concentration in alfalfa. Mean Se concentrations for the five cuttings on the 0.5, 1.0, and 2.0 kg/ha application rates were 1.49, 3.09 and 7.38 ppm, respectively, where only $BaSeO_4$ was applied, and 1.78, 3.51, and 5.27 ppm where $BaSO_4$ was added with $BaSeO_4$ to give a S/Se ratio of 1 (also see Table 2). When the S/Se ratio was increased to 10, Se concentrations were enhanced, particularly at the higher application rates (Table 2). This enhancement tended to disappear with time, especially at the low application rates. Reactions in the soil and leaching of selenate from the application zones and possibly beyond the root zone probably account for the decrease in effects with time. A crop response to the applied sulfate is not a likely explanation because no crop responses to S have been observed in the area of the study. The irrigation water supplies about three times the amount of S required by alfalfa each year. Yields were not measured because yield responses were not expected in this study.

The results of this study contrast somewhat with reports that applications of $BaCl_2$, $CaSO_4$, and S decreased Se availability to plants (10, 11, 16). These reports generally dealt with seleniferous soils or with soils treated with Se

Table 2—Se concentrations in alfalfa resulting from applications of BaSeO₄, CuSeO₄, and BaSeO₄—BaSO₄ mixtures to Portneuf silt loam

Se application rate	Carrier	S/Se	1966		1967		
			Cutting		Cutting		
			2nd	3rd	1st	2nd	3rd
kg/ha			Se concentration, ppm*				
0.0	Check	--	0.12	0.11	0.12	0.13	0.11
0.5	BaSeO₄	--	0.98	0.74	3.47	1.58	0.70
1.0	BaSeO₄	--	4.26	0.79	6.89	2.69	0.81
2.0	BaSeO₄	--	6.05	2.51	19.27	5.87	3.22
4.0	BaSeO₄	--	12.68	6.87	24.92	13.27	4.53
1.0	CuSeO₄	--	27.85	9.81	3.80	3.20	1.68
0.5	BaSeO₄ + BaSO₄	1	1.97	1.04	2.98	2.15	0.77
1.0	BaSeO₄ + BaSO₄	1	4.14	1.65	7.34	3.00	1.41
2.0	BaSeO₄ + BaSO₄	1	5.97	3.07	10.40	4.40	2.58
0.5	BaSeO₄ + BaSO₄	10	5.03	1.54	5.94	1.79	0.80
1.0	BaSeO₄ + BaSO₄	10	8.76	1.60	3.64	1.77	0.70
2.0	BaSeO₄ + BaSO₄	10	33.80	11.93	11.55	5.65	2.45

* Values are means of three replications. The coefficient of variation of the mean ranged from 4 to 52%, but were generally less than 30%.
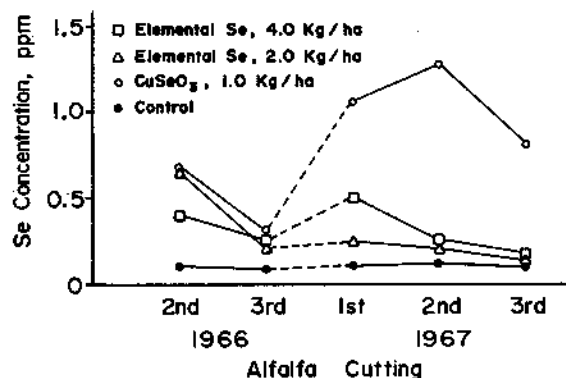
Fig. 1—Se concentration in alfalfa from $CuSeO_3$ and elemental Se applied to alkaline Portneuf silt loam. Points represent means of three replications. Standard error of the mean for successive cuttings are 0.168, 0.044, 0.088, 0.232 and 0.120, respectively, including data from both Fig. 1 and 2.

Fig. 2—Se concentration in alfalfa from two laboratory prepared ferric hydroxy bi-selenites applied to alkaline Portneuf silt loam. $(Fe)_x(OH)_y(HSeO_3)_z$ applied at 1.2 kg Se/ha and $(Fe)_a(OH)_b(HSeO_3)_c$ applied at 1.62 kg Se/ha. Points represent means of three replications. Standard error of the mean for successive cuttings are 0.168, 0.044, 0.088, 0.232, and 0.120, respectively, including data for both Fig. 1 and 2.

compounds from which plants absorbed relatively large amounts of Se. Our study was with a low Se, alkaline soil, and small applications of Se.

Se uptake from $CuSeO_4$ was initially very high and decreased in each successive crop (Table 2). All crops contained concentrations toxic to livestock except the third cutting in 1967. Thus, $CuSeO_4$ should not be used as a slowly available Se source for plants.

Selenites may be more useful than selenates as slowly available Se additives on alkaline soils. Se uptake from $CuSeO_3$ was in the protective and nontoxic range for livestock in all five crops (Fig. 1). Evidently $CuSeO_3$ provided only slow Se availability to alfalfa. The supply rate was not rapid enough to maintain the same Se concentrations in third cuttings as in second cuttings both years. The longer period of time between seasons was sufficient for more Se to become available to alfalfa, resulting in greater uptake the second year than the first (Fig. 1). $CuSeO_3$ does have potential as a slowly available Se source, but application rates should not exceed 1.0 kg Se/ha.

Maintenance of protective but nontoxic concentrations of Se in alfalfa grown in the greenhouse on some acid and neutral soils treated with $NaHSeO_3$ at rates of 1 ppm Se has been reported (5). Therefore, it may be that $CuSeO_3$ and $NaHSeO_3$ react in about the same way in the soil, even though $CuSeO_3$ is less soluble. Other selenites may behave similarly in the soil.

Elemental Se applied at 2.0 and 4.0 kg/ha provided adequate Se in alfalfa for livestock. Small amounts of the elemental Se became available rapidly after application to the soil, but later the availability decreased (Fig. 1). By the third cutting 1967, elemental Se at both rates supplied only slightly more Se to alfalfa than did the untreated soil. The low recovery of added elemental Se may render this form of Se impractical because of cost. It might be used at low rates of about ¼ or ½ kg/ha to provide Se for one or two crops. The elemental form is less hazardous to handle because it is rather inert and much less toxic to man than soluble forms.

The two ferric hydroxy bi-selenites provided slowly available Se to alfalfa, and resulting plant concentrations
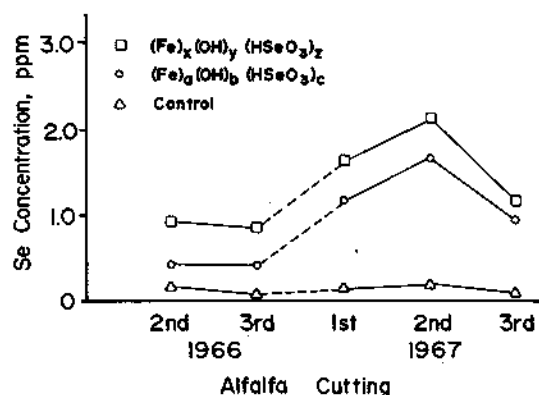
were in the desirable range for livestock in all five alfalfa crops (Fig. 2). The $(Fe)_a(OH)_b(HSeO_3)_c$ when applied at a higher rate provided less Se than did the $(Fe)_x(OH)_y(HSeO_3)_z$. Evidently Se from $(Fe)_x(OH)_y(HSeO_3)_z$ is more readily available than that from $(Fe)_a(OH)_b(HSeO_3)_c$. Both materials have potential as slowly available Se sources, but $(Fe)_a(OH)_b(HSeO_3)_c$ appears to have the greater potential because of its tendency to release Se at a slower, but adequate rate.

These laboratory-prepared bi-selenites may not be the same as those thought to be present in acid soils (7). Admittedly the compounds used are not well characterized, but neither are those forms present in soils. It is likely that different preparation procedures would produce compounds that differ considerably in their Se availability to plants. Nevertheless, the data reported in this paper indicate that compounds can be prepared that will provide a slowly available Se source for plants. How practical the preparation and use of these materials might be cannot be readily assessed. Furthermore, since these compounds appear to offer little advantage over $CuSeO_3$ and possibly other commercially available selenites, it may be more practical to use commercially available selenites.

In conclusion, the data presented in this paper show that Se uptake from $BaSeO_4$ on an alkaline soil is about the same as it is from soluble selenates. Addition of sulfate with the selenate may enchance Se uptake. Therefore it is not safe to add selenates to alkaline soils even when mixed with $BaSO_4$ because from these materials plants absorb Se concentrations toxic to livestock. Selenites can be safely added to the alkaline soil used in this study. Two ferric hydroxy selenites have potential as long-lasting, slowly available Se sources for plants, but they have little or no advantage over $CuSeO_3$. The possible advantages of selenites used in this study in comparison to a very soluble form such as Na_2SeO_3 were not directly determined. The most practical source will probably depend upon cost and convenience. Elemental Se can be safely added to the alkaline soil used but it is less efficient and therefore more expensive than selenite sources.

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